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Thin films of high temperature superconductors were made by sputtering a Westinghouse and by co-evaporation at the University of Texas. The former method produced thin films of YBaCuO which were completely superconducting at 82 K with 6 K transition widths. A new method was developed at the Universit of Texas which produced films of YBaCuO on strontium titanate that were superconducting at 84 K. This method minimizes the process temperature and produces films which are superconducting without the need for annealing. The films were also grown on silicon and sapphire substrates with zero resistance of 68 K or better.

A low temperature scanning tunneling microscope was used to study the superconducting properties of these and other samples. High quality spectroscopic data was obtained which yields a value of approximately 11 for the ratio of the superconducting gap to the transition temperature.

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ANNUAL REPORT
GRANT # AFOSR-87-0228
PI: Alex de Lozanne
University of Texas at Austin

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SUMMARY

Thin films of high temperature superconductors were made by sputtering at Westinghouse and by co-evaporation at the University of Texas. The former method produced thin films of YBaCuO which were completely superconducting at 82 K with 6 K transition widths. A new method was developed at the University of Texas which produced films of YBaCuO on strontium titanate that were superconducting at 84 K. This method minimizes the process temperature and produces films which are superconducting without the need for annealing. These films were also grown on silicon and sapphire substrates with zero resistances of 68 K or better. Critical currents at 4.2 K were greater than 10^4 A/cm^2 for films on silicon and greater than $7x10^5$ A/cm^2 for films on strontium titanate.

A low temperature scanning tunneling microscope was used to study the superconducting properties of these and other samples. High quality spectroscopic data was obtained which yields a value of approximately 11 for the ratio of the superconducting gap to the transition temperature

STATUS OF THE RESEARCH

Since the writing of the attached publications substantial progress has been made at the University of Texas. The composition of the films has been optimized with microprobe. Consequently the superconducting transitions are sharper and higher (84 K for as-deposited films), and the critical currents have improved by at least a factor of ten.

A system has been implemented that allows the transfer of a film from the synthesis chamber into the chamber of the scanning tunneling microscope, without any exposure to air. This is expected to improve the tunneling data substantially.

ARTICLES PUBLISHED WITH SUPPORT FROM THIS GRANT

"Sputter deposition of $YBa_2Cu_3O_{7-y}$ thin films"
R. M. Silver, J. Talvacchio and A. L. de Lozanne
Appl. Phys. Lett. **51**, 2149 (1987).

"As-deposited Superconducting Y-Ba-Cu-O Thin Films on Si, Al_2O_3 and $SrTiO_3$ Substrates"
R.M. Silver, A.B. Berezin, M. Wendman and A.L. de Lozanne
Appl. Phys. Lett., to appear June 20, 1988.

PROFESSIONAL STAFF

1) Supported by this grant:
   Richard M. Silver, graduate student
2) Not supported by this grant
   Alan Berezin, graduate student
   Logan Brashear, undergraduate student
   Prof. Alex de Lozanne, Principal Investigator

INTERACTIONS

Oral presentations on the synthesis of high temperature superconducting films and on tunneling into these materials were given as follows:

1) LT-18, Internat. Meeting of Low Temperature Physics, Kyoto, Japan, August 20-26, 1987.
2) March Meeting of the American Physical Society, New Orleans: March 21-25, 1988 (Two talks)
3) Meeting of the International Society for Hybrid Materials, April 12, 1988, Dallas, Tx.
4) Stanford University, June 10, 1988

NEW DISCOVERIES, INVENTIONS, PATENT DISCLOSURES

A patent application has been started for the thin film process developed at the University of Texas.

As-deposited superconducting Y-Ba-Cu-O thin films on Si, Al_2O_3, and $SrTiO_3$ substrates

R. M. Silver, A. B. Berezin, M. Wendman, and A. L. de Lozanne[a)]
Department of Physics, University of Texas, Austin, Texas 78712-1081

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We have developed an electron beam evaporator designed to deal with the special requirements of thin films of oxide superconductors. The growing surface is sprayed with plasma-excited oxygen while the sources and rate monitors operate in a low background pressure. This allows us to reproducibly grow films of Y-Ba-Cu-O on Si, Al_2O_3, and $SrTiO_3$ substrates at a substrate temperature of 540 °C which are superconducting without the need for annealing. The resistive transitions of most films show an onset of 90 K and zero resistance by 68 K. X-ray diffraction indicates a preferred orientation for growth on most Si and $SrTiO_3$ substrates. A preliminary measurement yields critical currents of at least 10^4 A/cm^2 at 4.2 K for a film on silicon.

Recently, there have been numerous reports[1] of techniques for growing thin films of the new oxide superconductors. This demonstrates not only the tremendous interest and importance of these films, but also the relative ease with which they can be synthesized (compared with the previous "high T_c" superconductors, namely, the *A*-15's). The new films have been grown by electron beam (*e*-beam) coevaporation[2-5] and sequential evaporation,[6] sputtering,[7-10] ion beam deposition,[11] molecular beam epitaxy,[12,13] laser ablation,[14] spray,[15] and spin-on[16] techniques. In all cases the films are deposited or post-annealed at temperatures above 600 °C (above 800 °C is most common). Only one group has reported a deposition temperature of 450 °C and no post-anneal,[10] but the fact that the substrates were immersed in a strong plasma discharge makes it likely that the substrates were actually at a higher temperature. We report here on a process that allows us to synthesize good quality films at temperatures below 550 °C. This process yields the highest transition temperatures reported for films on silicon substrates.

A low process temperature is desirable not only to avoid the problems already mentioned by Wu *et al.*,[14] but also to allow the growth of good films on practical substrates (i.e., other than $SrTiO_3$) or substrates with semiconductor devices. For scientific applications the capability of using different substrates is important since in many measurements (e.g., optical and rf) the properties of the substrate may obscure those of the film.

Most vacuum thin-film work to date involves the use of existing vacuum systems with only minor modifications. Large oxygen pressures, up to 10^{-3} Torr, have been used in vacuum chambers designed to operate at much lower pressures. The rates become irreproducible with high oxygen pressures because quartz-crystal rate monitors measure the mass deposited on them and therefore the measured rate depends on the degree of oxidation of the metal deposited on the monitor. Rate monitors of other types do not operate at all at such high pressures. Another potential problem due to high pressure is the scattering of the evaporant with the background gas, which not only alters the rates, but may also produce significant cross-talk between different rate monitors. Finally, *e*-beam sources arc at high pressures or have a severely reduced filament lifetime. Our design allows the operation of the sources and rate monitors at low pressure while the substrates receive a high flux of oxygen from a plasma source.

A schematic of our chamber is shown in Fig. 1. The chamber is divided into a main section that contains the sources and quartz-crystal rate monitors, and a smaller section that houses the substrates. The main section is pumped by a large (2700 ℓ/s) diffusion pump, yielding a base pressure of 10^{-7} Torr, while the substrate section is pumped by a 500 ℓ/s turbopump. The only connection between the two sections is a 9-cm-diam hole. During deposition, the oxygen pressure in the main section is 8×10^{-5} Torr, while the substrate section rises to 3 mTorr. The pressure at the substrate

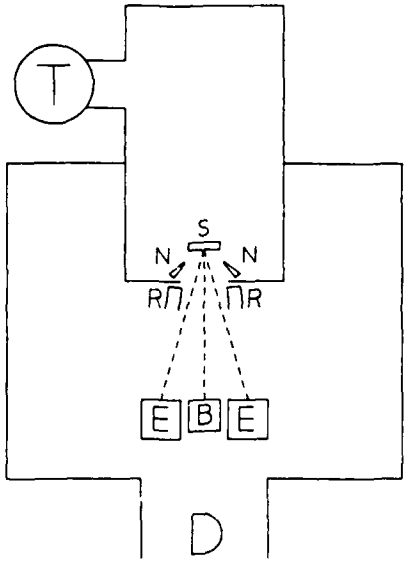

FIG. 1. Schematic of the chamber. The substrates (*S*) are in a subchamber pumped by a turbopump (*T*). Oxygen is sprayed on the substrate surface through two nozzles (*N*). The main part of the chamber, pumped by a diffusion pump (*D*), contains two electron beam sources (*E*), one evaporation boat (*B*), and three independent rate monitors (*R*) (only two are shown for clarity). The heating lamps, substrate rotation, and load-lock are not shown.

a) To whom all correspondence should be addressed.

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surface is estimated to be one order of magnitude higher since oxygen is fed through two glass nozzles directed towards the substrates. Glass is used to allow the creation of a plasma inside each nozzle by rf excitation. Approximately 250 W of rf power (14 MHz) is coupled with a coil wrapped around each nozzle.

We use two electron beam sources for yttrium and copper, and a resistively heated boat for barium. A feedback circuit uses the signals from independent quartz-crystal rate monitors to control the rate for yttrium and copper. A third rate monitor displays the barium rate, which is manually adjusted for drift.

The substrates are held tightly against a copper holder that is heated radiatively with quartz halogen lamps (the substrates are not exposed to the lamps). The temperature of a cavity in the copper holder is measured with a pyrometer which has been calibrated against two thermocouples. This cavity is completely shielded from the radiation coming from the lamps, thus avoiding any possible effect on the pyrometer reading. The substrate holder is loaded through a load-lock and is rotated during deposition. The load-lock not only improves the turnaround time, but will also allow us to measure films that have never been exposed to air with a low-temperature scanning tunneling microscope.[17] Further details of the deposition chamber will be given elsewhere.

The films described here were deposited on Si(111) (orientation is not important since the native oxide was not removed), $Al_2O_3(1\bar{1}02)$ (*R*-plane), and $SrTiO_3(100)$ substrates at a temperature of 540 °C and a rate of 0.6 nm/s for a total thickness of 700 nm. The substrates were rotated at 6 rpm during deposition. After deposition the substrate temperature was lowered to 400 °C for 20 min, with the plasma spray and rotation still on. The samples were then pulled into the load-lock and allowed to cool in one atmosphere of pure oxygen. The samples were handled in a nitrogen atmosphere as much as possible to prevent damage from moisture.[9]

The composition according to wavelength dispersive spectroscopy ("microprobe") is $YBa_{1.72}Cu_{3.16}O_{7-y}$. While this measurement has been calibrated with bulk metal and oxide standards, the measured composition of the thin film has to be corrected because of the fact that part of the signal comes from the substrate. We estimate a total uncertainty of about 4 at. %. We expect to grow better films once we determine the composition more accurately. Our run-to-run reproducibility is better than the resolution of energy dispersive spectroscopy (EDS or EDX) and is estimated to be a few percent. With two different runs we find good reproducibility of the superconducting transitions among all samples, without much difference due to the type of substrate.

The resistive transitions of films on Al_2O_3, Si, and $SrTiO_3$, shown in Fig. 2, were measured with a 20 μA (peak-to-peak) excitation current and a lock-in amplifier. The resistivity scales were calibrated with van der Pauw measurements at 100 and 300 K. Contact resistance was always below 200 Ω. The film in Fig. 2(a) shows a sharp transition with an onset of 90 K, zero resistance below 68 K, and a width (10–90%) of 16 K. Although this film was deposited on Si, Fig. 2 shows that all three substrates yield very similar

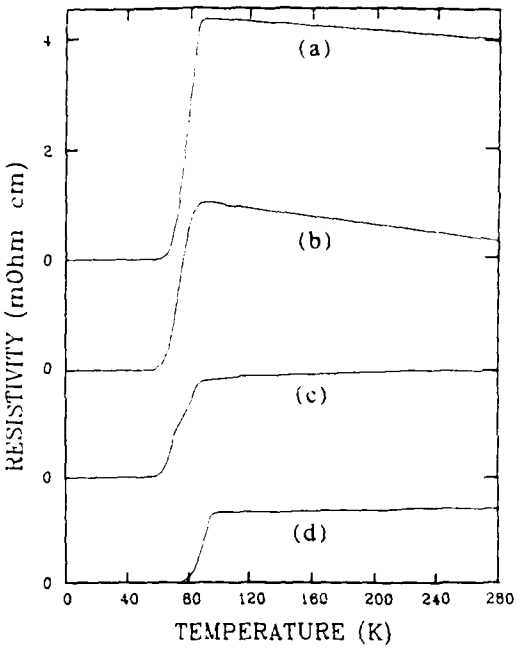

FIG. 2. Resistivity vs temperature for three as-deposited $YBa_2Cu_3O_{7-y}$ films on (a) silicon, (b) sapphire, and (c) $SrTiO_3$ substrates. After annealing at 860 °C for 2 h the latter film improved, as shown in (d).

resistivity versus temperature curves. The high resistivities above 100 K are attributed to being off stoichiometry. A preliminary measurement yields critical currents of at least 10^4 A/cm^2 at 4.2 K for a film on silicon.

We performed experiments to determine the effect of annealing at 450 and 860 °C. Samples on Si, Al_2O_3, and $SrTiO_3$ were annealed at 450 °C for 1 h and then slowly cooled to room temperature. The samples on Si and Al_2O_3 showed no change in the resistivity versus temperature characteristics, while the transition width of the $SrTiO_3$ sample was 2° narrower. These measurements indicate that we are incorporating a sufficient amount of oxygen in the films during the deposition process. A $SrTiO_3$ sample was annealed at 860 °C for 2 h and then slowly cooled to room temperature. After annealing the film showed zero resistivity at 78 K, an improvement of 8 K, and a transition width of 8 K. The fact that the films do not have zero resistivity above 78 K indicates that they are off stoichiometry. Since the transition was narrower after a high-temperature anneal, the as-deposited structure can be improved. Fine tuning the plasma strength, oxygen pressure, and substrate temperature is likely to improve the structure by increasing the volume of superconducting material.

Figure 3 shows x-ray diffraction patterns for samples on Si and $SrTiO_3$ substrates (same as in Fig. 2). The advantage of using a silicon substrate is that there is no overlap between the (020) peak of $YBa_2Cu_3O_{7-y}$ and the substrate peaks. This x-ray pattern shows the (020) peak at $2\theta = 46.7°$, as well as the (005) peak and the dominant peak of the polycrystalline orthorhombic phase at 32.8°. The relative heights of these peaks indicate that this sample shows a preferred orientation with a mixture of *b* and *c* axes growth perpendicular to the substrate. The x-ray pattern in Fig. 3(b) shows

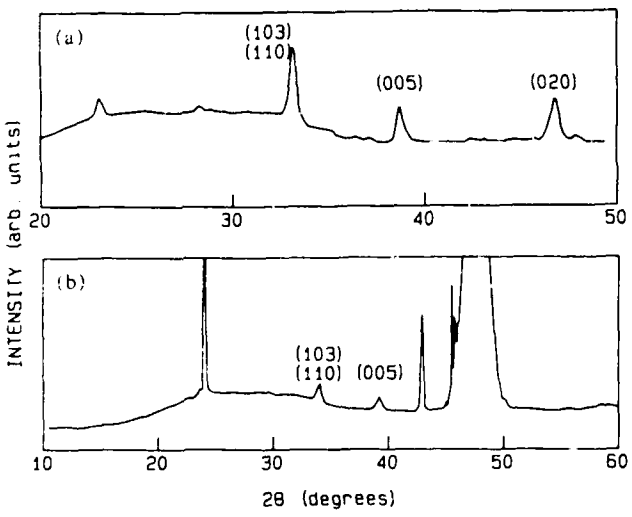

FIG. 3. Top: X-ray diffraction pattern of a film on a silicon (111) substrate without post anneal (same as in Fig. 2). Bottom: Similar pattern of a film on a $SrTiO_3$ substrate. Only $YBa_2Cu_3O_{7-y}$ peaks have been labeled; the rest belong to the substrate as confirmed by a similar pattern without the film.

that the growth on $SrTiO_3$ was partially oriented in the *c* axis direction. X-ray data of depositions on sapphire substrates showed that the growth had no preferred orientation.

More recently, we have obtained as-deposited films which have zero resistivity as high as 84.5 K on $SrTiO_3(110)$. These films were deposited at a substrate temperature of 570 °C and had a composition of $YBa_{2.02}Cu_{3.08}O_{7-y}$. Films on Al_2O_3, Si, and $SrTiO_3(100)$ deposited in the same runs as the $SrTiO_3(110)$ samples showed zero resistivity usually around 68 K. We have also deposited films in the $Y_2Ba_4Cu_8O_{20-y}$ structure.[18] These films show an onset at 81 K and are completely superconducting by 78 K. Details of the more recent work as well as our current study of deposition parameters will be published elsewhere.

In summary, we have developed a process that yields the highest superconducting transition temperatures for films deposited on silicon substrates and properties that are not strongly dependent on the substrates used when deposited at 540 °C. We expect this process to apply to most of the oxide superconductors and, in particular, to the new bismuth-based materials.[19]

We gratefully acknowledge the recent donation by Motorola Inc. of the evaporator used in this experiment. We are also indebted to H. Steinfink, R. H. Hammond, J. Talvacchio, and K. R. Carter for useful discussions, S. Sutton for assistance with energy and wavelength dispersive spectroscopy, L. Brashear and L. Deavers for technical assistance, and J. Erskine, J. Thompson, M. Fink, and K. R. Carter for borrowed equipment. This work is supported by the Air Force Office of Scientific Research (87-0228) and National Science Foundation (DMR-855305), with matching contributions from IBM, Texas Instruments, Bell Communications Research, Kodak, and the Microelectronics and Computer Technology Corporation (MCC).

[1]Over 100 papers have been published on thin films of the new oxide superconductors. For brevity we reference only a few representative examples.
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Sputter deposition of $YBa_2Cu_3O_{7-y}$ thin films

R. M. Silver[a] and J. Talvacchio
Westinghouse R&D Center, Pittsburgh, Pennsylvania 15235

A. L. de Lozanne
Department of Physics, University of Texas, Austin, Texas 78712

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Thin films of $YBa_2Cu_3O_{7-y}$ were prepared by magnetron sputtering. The films were characterized by x-ray diffraction, *in situ* x-ray photoelectron spectroscopy to determine the as-deposited oxygen content for various substrate temperatures, and scanning electron microscopy to analyze the microstructure. The orthorhombic phase was observed after an *ex situ* 700 °C anneal. We have obtained films which were completely superconducting at 82 K with 6 K transition widths.

Recent discoveries of high-temperature superconductivity in perovskite-related oxides have generated tremendous interest in these materials.[1,2] For scientific and technological reasons the study of sputtered[3-5] and evaporated[6-11] films is of interest. Recent papers have been published on evaporated films which were completely superconducting at 90 K and had transition widths of a few degrees. These films all required *ex situ* anneals of greater than 850 °C. However, there have been recent reports on sputtered films which were superconducting with no post anneal.[12]

In this letter, we report on thin films 0.5–0.8 μm thick prepared by magnetron sputtering from three metallic sources. The films were made in one chamber of a four-chamber ultrahigh vacuum deposition and analysis system which has been previously described.[13] Yttrium and barium were sputtered from rf guns and copper from a dc gun. As shown in Fig. 1, there were four sputter guns in a plane each spaced 60°–120° apart. The sample was rotated from gun to gun with a 3-s delay in front of each gun yielding a layered structure. Each layer was approximately one monolayer (0.2 nm) thick resulting in a net deposition rate of 5.0 nm/min. We operated with 1.3×10^{-3} Pa of oxygen and 2.1 Pa of argon in a chamber which had a base pressure of 10^{-6} Pa. The substrates used were $SrTiO_3(100)$ and $Al_2O_3(11\bar{2}0)$.

We used *in situ* x-ray photoelectron spectroscopy (XPS) to determine the as-deposited oxygen content, $7-y$, of several films. Peak areas from O_{1s}, Y_{3d}, $Ba_{3d\,5/2}$, and $Cu_{2p3/2}$ photoelectrons were normalized for the calculation of composition with normalization factors based on measurements of single-metal oxides. The results for different substrate temperatures are shown in Fig. 2. The maximum oxygen content occurred for a substrate temperature of 400 °C. However, the oxygen content was nearly independent of substrate temperature between room temperature and 700 °C. For a deposition temperature of 800 °C, the oxygen content was approximately five times smaller than for lower temperatures. Electron microprobe measurements confirmed that the overall oxygen content of films deposited at 400 °C was greater than 50 at. %. Therefore, a sufficient amount of oxygen was present to form the orthorhombic phase of $YBa_2Cu_3O_{7-y}$. However, x-ray data showed that with a 400 °C substrate temperature, there was no orthorhombic phase or other crystalline phase present in the as-deposited films. Films deposited with substrate temperature $\geqslant$700 °C were crystalline, but no effort was made to obtain the correct ratio of metallic constituents. We concentrated on obtaining the correct composition of metallic elements in the amorphous films deposited at 400 °C since they had the highest oxygen content.

X-ray analysis was performed on samples held in air in an x-ray diffractometer. The results showed that the as-deposited films were amorphous. In the case of annealed samples, the amorphous films grown at 400 °C on Al_2O_3 substrates were transferred directly to a preheated furnace. The samples were annealed in flowing oxygen for 3 min at temperatures varying from 600 to 900 °C and then slowly cooled to room temperature. Figures 3(a), 3(b), and 3(c) show that the orthorhombic phase was present after anneals of 900, 800, or 700 °C. However, Fig. 3(d) shows that the orthorhombic phase was not present after a 600 °C anneal. The resistive superconducting transitions were broad after 700,

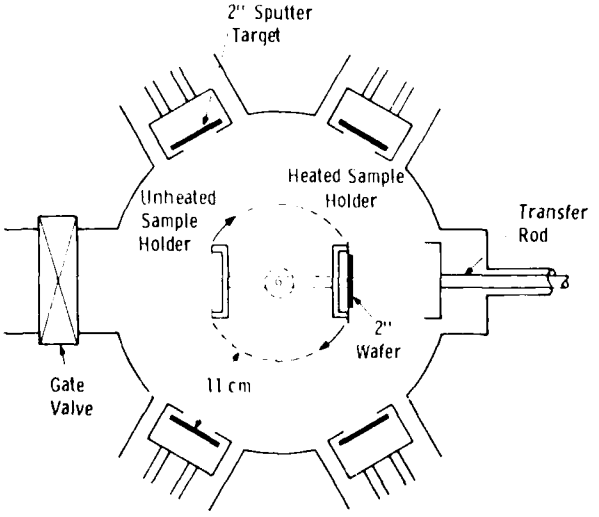

FIG. 1. Schematic of a cross section of the sputtering chamber.

[a] Permanent address: Department of Physics, University of Texas, Austin, TX 78712.

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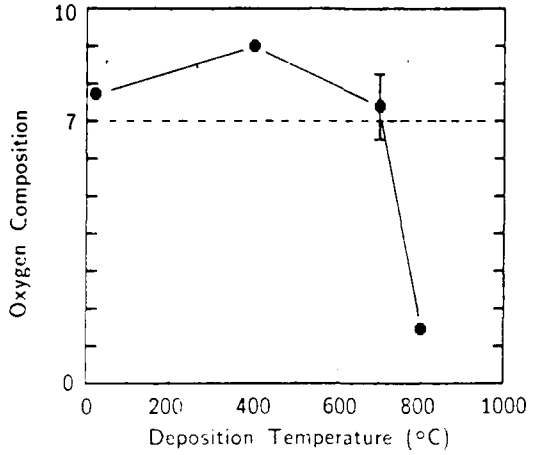

FIG. 2. Oxygen content of as-deposited films determined by *in situ* XPS

800, or 900 °C anneals. The transition widths were similar to those of other films deposited on Al_2O_3 substrates and annealed at 850 °C.[14] We suppose that it was the presence of large amounts of oxygen or of a truly amorphous structure in the as-deposited films that allowed the orthorhombic phase to form at a temperature between 600 and 700 °C since other reports indicated that a higher annealing temperature was required.[5,7,8] In contrast to the post-annealing results in the literature, films that were deposited at temperatures of 650 or 700 °C grew in the perovskite-related structure.[4,13] In addition to diffractometer peaks due to the orthorhombic phase, a single, minor peak was usually present that was tentatively attributed to barium. The presence of a second, minor phase may have been due to either deviations from stoichiometry, exposure to air, or substrate/film interdiffusion.

Scanning electron microscopy (SEM) was used to observe the microstructure of films before and after annealing. Films on $SrTiO_3$ and Al_2O_3 were analyzed; some with minimum exposure to air and others with no precautions against air exposure. Figure 4(a) shows a film on Al_2O_3 before annealing in which no handling precautions were taken; the film was severely cracked. The film damage occurred after

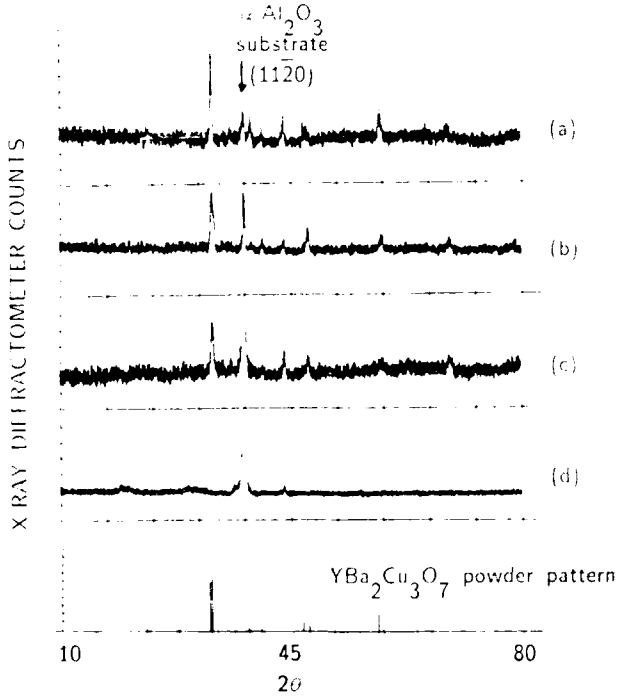

FIG. 3. X-ray data for films deposited at 400 °C on Al_2O_3 substrates. The orthorhombic phase was present after (a) 900 °C, (b) 800 °C, or (c) 700 °C anneals. As-deposited films or films annealed at (d) 600 °C were amorphous.

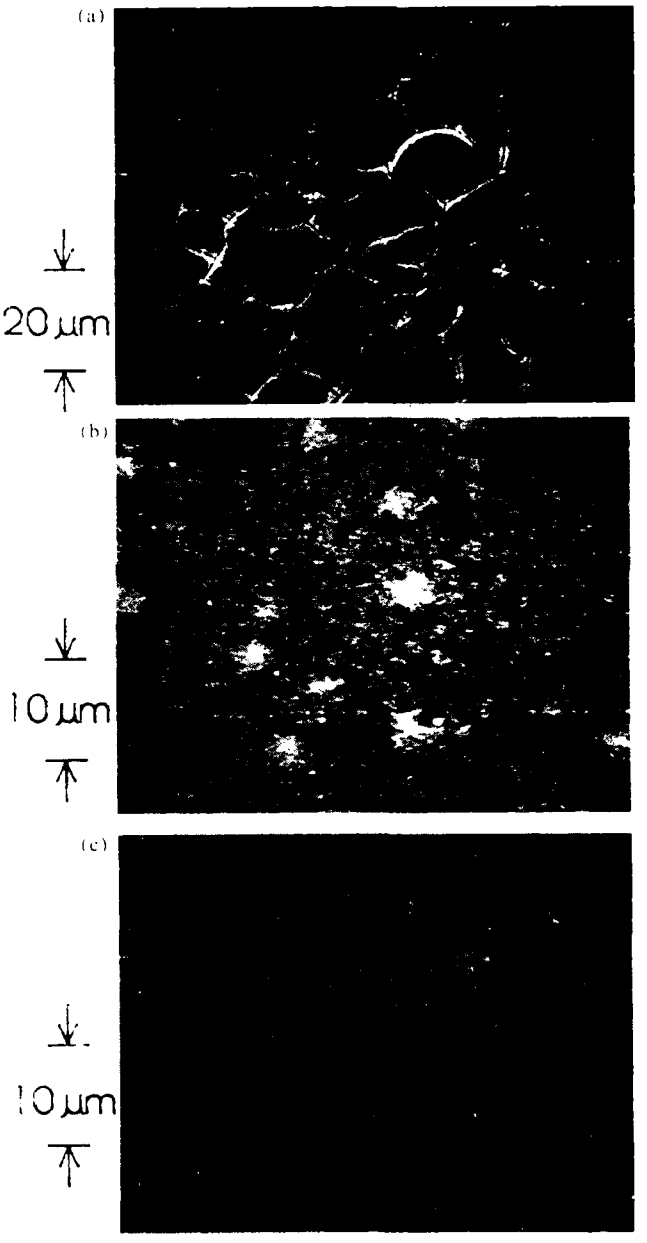

FIG. 4 (a) shows a scanning electron micrograph of a film on Al_2O_3 before annealing and after having been exposed to air. Another film (b), similar to that in (a), was handled exclusively in nitrogen. A third film (c), shown after an *ex situ* anneal, was also handled in nitrogen and was microscopically smooth. EDS results of the dark blotches on the surface of the film in (c) showed that the blotches were primarily copper. Some films were perfectly smooth and featureless at this magnification.

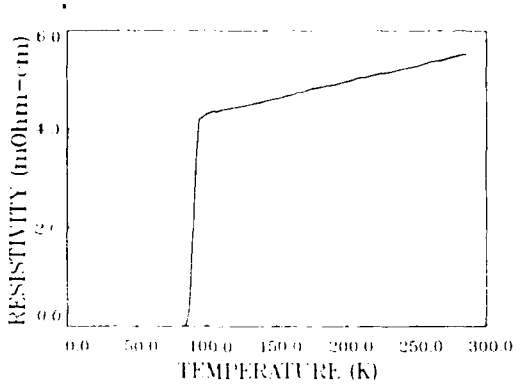

FIG. 5. Resistivity vs temperature for a sputtered $YBa_2Cu_3O_{7-\delta}$ film on $SrTiO_3$ annealed at 860 °C for 1 h.

about 10–15 min exposure to air. Energy dispersive spectroscopy (EDS) of the cracks detected only Al_2O_3, which showed that the cracks extended through to the substrate. After annealing at 900 °C, the film used for Fig. 4(a) had a resistively measured transition width of 40 K. Other films grown on Al_2O_3, such as that used for Fig. 4(b), were handled exclusively in dry nitrogen, exhibited no cracking, and had superconducting transition widths of 15 K. Films grown on $SrTiO_3$ showed considerably less cracking than those on Al_2O_3. Figure 4(c) shows a film on sapphire after annealing which was handled in dry-nitrogen glove bags. It was microscopically smooth. Exposure to air after annealing caused less microstructural damage. The primary degradation seems to have been a loss of oxygen because, in most samples, a 400 °C anneal in oxygen restored the original superconducting qualities. X-ray analysis of a sample exposed to air for 4 h after having been annealed showed the formation of a second phase of barium carbonate and no detectable hydroxides.

Our best films were grown on $SrTiO_3$ at a substrate temperature of 400 °C. After annealing in flowing oxygen for 1 h at 860 °C, the samples were slowly cooled to room temperature. The films had transition onsets above 91 K and 5–95% transition widths of 6 K. Figure 5 is a curve of resistivity versus temperature for one of these films. There was a compositional phase spread of about 10 at. % for each metallic constituent across a 50-mm-diam sample holder. The transition widths varied from 6 K for the 6 × 6 mm samples, which had a composition closest to the $YBa_2Cu_3O_{7-\delta}$ stoichiometry, to 50 K for those farthest from stoichiometry. Room-temperature resistivities were generally between 1 and 6 Ω cm. Using a vibrating-sample magnetometer, we measured critical currents of 2×10^5 A/cm^2 at 4.2 K and 1×10^4 A/cm^2 at 70 K. An x-ray texture camera diffraction pattern indicated that the films were polycrystalline with no preferred orientation. We suppose there was no preferred orientation because the substrates were degassed at 900 °C and our later reflection high-energy electron diffraction (RHEED) data did not show a good single-crystal $SrTiO_3$ pattern until the substrates had been heated to > 1100 °C. We attributed the high room-temperature resistivities to the polycrystalline microstructure of the samples. This was based on recent papers which report a large anisotropy of the room-temperature resistivity between the (110) and the (001) directions in highly oriented films.[4] A random polycrystalline orientation would be expected to yield a resistivity which was an average of the (110) and (001) values.

In summary, we have sputtered polycrystalline films which were completely superconducting at 82 K with critical currents of 2×10^5 A/cm^2 at 4.2 K. We have found that the oxygen content in as-deposited films was nearly independent of substrate temperature < 700 °C and that the orthorhombic phase was present after annealing at 700 °C. Microscopic cracking that occurred in films which were grown on Al_2O_3 and exposed to air was reduced by growing films on $SrTiO_3$ and eliminated by handling the samples in dry-nitrogen glove bags.

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